

**OCEAN ALKALINITY AND THE CRETACEOUS/TERTIARY BOUNDARY;** K.G. Caldeira, and M.R. Rampino, Earth Systems Group, Dept. of Applied Science, New York University, 26 Stuyvesant St., New York, NY 10003.

A biogeochemical cycle model resolving ocean carbon and alkalinity content is applied to the Maestrichtian and Danian. The model computes oceanic concentrations and distributions of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\Sigma\text{CO}_2$ . From these values an atmospheric  $\text{pCO}_2$  value is calculated, which is used to estimate rates of terrestrial weathering of calcite, dolomite, and calcium and magnesium silicates. Metamorphism of carbonate rocks and the subsequent outgassing of  $\text{CO}_2$  to the atmosphere are parameterized in terms of carbonate rock reservoir sizes, total land area, and a measure of overall tectonic activity, the sea-floor generation rate.

The ocean carbon reservoir computed by the model is used with DSDP  $\delta^{13}\text{C}$  data to estimate organic detrital fluxes under a variety of ocean mixing rate assumptions. Using Redfield ratios, the biogenic detrital flux estimate is used to partition the ocean carbon and alkalinity reservoirs between the mixed layer and deep ocean. The calcite flux estimate and carbonate ion concentrations are used to determine the rate of biologically mediated  $\text{CaCO}_3$  titration.

Short-term ( $< 20$  kyr) changes after the boundary are not well constrained by the model, but a number of considerations argue for a short-term increase in atmospheric  $\text{pCO}_2$  (e.g., rapid ocean mixing, acid rain, possible  $\text{CO}_2$  releases by bolide impact). Following this possible short-term increases in  $\text{pCO}_2$ , atmospheric  $\text{pCO}_2$  may have fallen due to an "alkalinity crisis".

Oceanic productivity was severely limited for approximately 500 kyr following the K/T boundary such that the total calcite shell production rate fell below the rate of riverine  $\text{Ca}^{2+}$  input to the ocean, resulting in significant increases in total ocean alkalinity. Model results suggest that the effects of increased ocean alkalinity on atmospheric  $\text{pCO}_2$  were partially offset by the drastic weakening of the biological carbon pump which resulted in larger  $\Sigma\text{CO}_2$  increases in the mixed-layer than in the deep ocean. However, mixed-layer alkalinity increased more than  $\Sigma\text{CO}_2$  on 100 kyr time-scales, and the overall picture is one of a major imbalance in ocean alkalinity.

Prior to the full recovery of biogenic calcite precipitation, results indicate that metamorphic releases of  $\text{CO}_2$  began to balance the increased ocean alkalinity, raising surface  $\text{pCO}_2$  near to pre-boundary levels. As productivity returned to the ocean, excess carbon and alkalinity was removed from the ocean as  $\text{CaCO}_3$ , removing two equivalents of alkalinity for each mole of carbon. Model runs indicate that this resulted in a transient imbalance in the other direction, i.e., there was an excess of ocean carbon which may have resulted in a transient increase in atmospheric  $\text{pCO}_2$  around 65 mybp. Ocean chemistry returned to near-equilibrium by about 64 mybp.

Existing biogeochemical models, including this one, have severe limitations. Major uncertainties exist in the parameterizations of rates of weathering and metamorphism on the time-scales investigated with this model. Organic carbon burial rates continue to be problematic. However, mathematical models of the biogeochemical consequences of global catastrophes in earth history have the advantage of being fully explicit with regard to both processes and parameterizations, making the models internally consistent and falsifiable.